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(54) PROCESS FOR HYDROGENATING NAPHTHALENE AND ALKYLNAPHTHALENES

(71) We, INSTITUT FRANCAIS DU PETROLE, formerly Institut Francais du Pétrole, des Carburants et Lubrifiants, a French body corporate, of 4 Avenue de Bois-Preau, 92502 Rueil-Malmaison, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns a process for hydrogenating naphthalene and alkylnaththalenes to form tetrahydronaphthalene or alkyltetrahydronaphthalenes.

The hydrogenation of naphthalene to tetrahydronaphthalene in the presence of catalysts derived from a transition metal compound and aluminium derivatives, of the Ziegler type, has already been proposed. The performance of such catalysts is irregular and they do not permit tetrahydronaphthalene with a purity degree higher than 99.5% to be obtained.

It has now been discovered that it is possible to improve the procedure for making such catalysts.

According to the invention there is provided a process for preparing tetrahydronaphthalene or an alkyltetrahydronaphthalene by contacting hydrogen with naphthalene or an alkylnaphthalene in the presence of a cobalt-containing catalyst, in which the catalyst has been prepared in the absence of naphthalene and alkylnaphthalene by adding a solution of at least one cobalt salt to at least one trialkylaluminium compound and/or alkylaluminium hydride, in the liquid phase, and heating the mixture during the admixing period or thereafter to a temperature in the range 50° to 200°C, the resulting catalyst being admixed with the naphthalene or alkylnaphthalene to be subjected to hydrogenation only thereafter.

The procedure used to prepare the catalyst has a great importance when the catalyst is to be used for hydrogenating naphthalene or alkylnaphthalenes, even though, for the hydrogenation of other unsaturated compounds, for example olefins, the effect of the procedure on the activity of the catalyst is not substantial.

It is essential to the present process to manufacture the catalyst before contacting the same with naphthalene or alkylnaphthalene and it is preferred to manufacture the catalyst in a sufficiently concentrated medium: for example a medium containing at least 0.1% by weight of cobalt in the form of a salt and at least 0.1% by weight of aluminium in the form of a trialkylaluminium or alkylaluminium hydride, with respect to the weight of catalyst solution produced, the upper limit corresponding to saturation. Once the catalyst has been prepared, it may, without inconvenience, be diluted into the naphthalene to be subjected to hydrogenation, and cobalt concentrations of from 5 to 300 ppm by weight with respect to the naphthalene or alkylnaphthalene may advantageously be used.

Other preferred conditions of the process are indicated below:

(a) The rate of addition of the cobalt solution to the alkyl aluminium compound or the alkyl aluminium hydride, may vary in a wide range, provided however that a too high temperature increase is avoided; this addition may be performed for example over a period of from 1 minute to 6 hours.

(b) Suitable cobalt salts are for example cobalt salts of carboxylic acids having from 3 to 40 carbon atoms, e.g. cobalt octoate, cobalt naphthenate, or cobalt stearate, or cobalt alcoholates such as cobalt acetylacetonates.

The degree of purity of the salt is not critical and the cobalt content of the commercially available solutions may vary for example from 2 to 25% by weight. It is however preferable to use salts having a cobalt content of at least 6%.

As solvent for the cobalt salt, it is possible to use an aliphatic or cycloaliphatic saturated hydrocarbon which is a liquid at the temperature of the catalyst manufacture, and contains for example from 5 to 20 carbon atoms. Suitable such solvents are for example *n* - hexane, *iso*octane, *n* - decane and *n* - hexanedecane.

Tetrahydronaphthalene or decahydronaphthalene may also be used.

(c) The trialkylaluminium compound or alkylaluminium hydride may be used in a pure state, or as a solution in a solvent, such as tetrahydronaphthalene. Suitable aluminium compounds are for example triethylaluminium, tri*iso*butyl aluminium, di*iso*butylaluminium hydride, and trioctylaluminium. For example, the aluminium compound may be of the formula $AlR_1R_2R_3$ in which R_1, R_2, and R_3, which may be identical to or different from each other, are hydrocarbon monovalent radicals, each having from 2 to 10 carbon atoms.

(d) During the manufacture of the catalyst, the solution of the cobalt salt is added, for example by pouring, into the trialkylaluminium or alkylaluminium hydride in the liquid phase, the reverse procedure being excluded, since it does not result in an active and selective catalyst.

(e) During or after the period of mixing of the two catalyst components, the resulting mixture is heated up to a temperature of from 50° to 200°C, preferably from 110° to 170°C. The heating period is preferably from 5 minutes to 24 hours.

The catalyst manufacture is preferably conducted in the absence of water and oxygen, and can for example be carried out under a gas such as hydrogen, nitrogen, argon, methane or a mixture thereof.

The resulting catalyst is stable over a long period and is capable of giving higher velocity and selectivity in the process than catalysts obtained up to now.

The ratio by volume of the concentrated catalytic solution to the reaction medium may vary, for example, from 0.01% to 10% and preferably from 0.05% to 5%. The atomic ratio of aluminium to cobalt in the alkylaluminium compound and the cobalt salt used to prepare the catalyst is preferably in the range 2:1 to 4:1 and more preferably in the range 2.5:1 to 3.5:1.

By the use of the process of the invention catalysts of high activity can be prepared, making it possible to use cobalt concentrations of as low as a few parts of cobalt per million of parts by weight of compound to be hydrogenated, the preferred cobalt concentrations being in the range 5 to 300 parts per million.

The hydrogenation temperature is in the range 90° to 200°C, preferably from 110° to 180°C. The hydrogen partial pressure is from 0.1 to 50 bars, preferably from 0.5 to 30 bars.

An increase of the hydrogen partial pressure makes it possible to reduce the duration of the hydrogenation. For pressures higher than 5 bars, although the rate of hydrogenation of tetrahydronaphthalene to decahydronaphthalene is low, a certain amount of decahydronaphthalene may be formed.

As naphthalene there can be used naphthalene from coal or of petrochemical origin, whose sulfur content is lower than 10 parts per million.

The following examples illustrate the invention without however limiting its scope.

EXAMPLE 1

A catalyst was prepared as follows. 1.2 mmole of triethylaluminum was dissolved in 5 ml of tetrahydronaphthalene, and heated to 140°C. Into this mixture we progressively pour (over about 10 minutes) with stirring, 0.4 mmole of cobalt octoate dissolved in 5 ml of tetrahydronaphthalene. The reduction of the cobalt salt took place at 140°C and the catalyst formed was withdrawn and injected into an autoclave preliminarily cleared of water and oxygen and containing 270 g of naphthalene, distilled over sodium and maintained at 140°C. Hydrogen was introduced at a pressure of 3 bars and stirring was performed. The reaction started and continues at a constant rate under 3 bars pressure. After 51 minutes at 140°C, the reaction rate had considerably diminished and the tetrahydronaphthalene withdrawn had a purity of 99.85% and contained about 100 ppm of catalyst. The yield was quantitative.

EXAMPLE 2
(comparative)

Example 1 was repeated, except that the order of introduction of cobalt octoate and triethylaluminum was reversed. After 1 hour, the conversion of naphthalene to tetrahydronaphthalene only amounted to 5% showing that the activity of the catalyst so prepared was very low.

EXAMPLE 3

Example 1 was repeated, but with the use of a solution containing 50% of triethylaluminum in decahydronaphthalene and a commercially available cobalt salt solution containing 12.4% by weight of cobalt. In this way, a larger amount of catalyst was prepared. The hydrogenation of naphthalene took place in 1 hour with an amount of catalyst corresponding to 100 ppm by weight of cobalt; the product had the same characteristics as in Example 1; the yield was quantitative.

EXAMPLE 4

Example 1 was repeated by injecting a catalyst which has been prepared according to example 3, four months previously. Naphthalene was hydrogenated by means of a portion of this catalyst corresponding to 100 ppm of cobalt; the product has the same purity as in Example 1. The yield was quantitative.

This example shows the stability of the catalyst so prepared.

EXAMPLE 5
(comparative)

Example 1 was repeated, except that the triethylaluminum solution was not heated during the manufacture of the catalyst, which was instead conducted at 20°—40°C. After 1 hour of reaction, the conversion of naphthalene only amounted to 5%; this example shows the very important effect of the heating during the catalyst manufacture when the latter is in the form of a relatively concentrated solution.

EXAMPLE 6

Example 1 was repeated except without heating during the reduction period, but by instead heating the catalyst thereafter for 10 minutes at 140°C, before its injection into the naphthalene. Hydrogenation of the latter was performed in 1 hour and the resulting product had the same characteristics as that of Example 1. The yield was quantitative.

EXAMPLE 7

Example 1 was repeated but with the introduction of only 50 ppm of catalyst. The reaction took place in 2 hours, and the tetrahydronaphthalene withdrawn had a purity of 99.9%. The yield was quantitative.

EXAMPLE 8

Example 7 was repeated, but with the introduction of only 25 ppm of catalyst. The reaction took place in 4 hours and the resulting product had the same characteristics as in Example 7. The yield was quantitative.

EXAMPLE 9

Example 1 was repeated, except that 1.6 mmole of triethylaluminium was used in the catalyst preparation. In this case, the conversion of naphthalene was 25% after 1 hour.

EXAMPLE 10
(comparative)

Example 1 was repeated but with the use of 0.3 mmole of nickel in the form of nickel octoate. The conversion after 1 hour was only 10%.

EXAMPLE 11
(comparative)

Example 2 was repeated but with the use of 0.3 mmole of nickel in the form of nickel octoate. The conversion after 1 hour was only 10%.

Examples 10 and 11 show that catalysts prepared from nickel salts are less active than those prepared from cobalt and that, when using a nickel salt, the order of introduction of the catalyst components has no influence on the activity of the resulting catalyst.

EXAMPLE 12

Example 1 was repeated, but with only 10 ppm of catalyst and under a pressure of 10 bars. The reaction took place in one hour and a half and the tetrahydronaphthalene produced had the same purity as the product in Example 1.

The yield was quantitative.

EXAMPLE 13

Example 1 was repeated, except that the naphthalene was replaced by its higher homolog β - methylnaphthalene. After an hour and a half of reaction, the resulting product was analyzed. It contained 40.9% of 2 - methyltetrahydronaphthalene, 55.7% of 6 - methyltetrahydronaphthalene and about 3% of methyldecahydronaphthalene; the β - methylnaphthalene had been entirely converted.

EXAMPLE 14

Example 13 was repeated but with the use of a mixture containing about 35% of α - methylnaphthalene and 65% of β - methylnaphthalene. After hydrogenation, the resulting product was analyzed. It contained 38.4% of 1 - methyl - tetrahydronaphthalene, 41.7% of 6 - methyltetrahydronaphthalene, 19.3% of 5 - methyltetrahydronaphthalene and 0.3% of methyldecahydronaphthalene.

In the preceding examples, the product obtained may be separated from the traces of catalyst contained therein by known methods, for example, distillation or passage over an adsorbing bed.

WHAT WE CLAIM IS:—

1. A process for preparing tetrahydronaphthalene or an alkyltetrahydronaphthalene by contacting hydrogen with naphthalene or an alkylnaphthalene in the presence of a cobalt-containing catalyst, in which the catalyst has been prepared in the absence of naphthalene and alkylnaphthalene by adding a solution of at least one cobalt salt to at least one trialkylaluminium compound and/or alkyl aluminium hydride, in the liquid phase, and heating the mixture during the admixing period or thereafter to a temperature in the range 50° to 200°C, the resulting catalyst being admixed with the naphthalene or alkylnaphthalene to be subjected to hydrogenation only thereafter.

2. A process according to claim 1, in which the cobalt salt and aluminium compound concentrations during the catalyst preparation correspond respectively to at least 0.1% of cobalt and at least 0.1% of aluminium by weight with respect to the weight of the catalyst solution produced.

3. A process according to claim 1 or 2, used for hydrogenating naphthalene to produce tetrahydronaphthalene.

4. A process according to claim 1, 2, or 3, wherein the cobalt salt and aluminium com-

pound or compounds are used in such proportion that the atomic ratio of aluminium to cobalt is in the range 2:1 to 4:1.

5. A process according to claim 4, in which the atomic ratio of aluminum to cobalt is in the range 2.5:1 to 3.5:1.

6. A process according to any one of claims 1 to 5, in which the heating step in the preparation of the catalyst is performed over a period of from 5 minutes to 24 hours.

7. A process according to any one of claims 1 to 6, in which the addition of the solution of the cobalt salt to the aluminium compound is carried out over a period in the range 1 minute to 6 hours.

8. A process according to any one of claims 1 to 7, in which the heating step in the preparation of the catalyst is performed at a temperature in the range 110°—170°C.

9. A process according to any one of claims 1 to 8, in which the hydrogenation is conducted at a temperature in the range 90°—200°C.

10. A process according to any one of claims 1 to 9, in which the ratio by volume of the catalyst solution to the reaction volume is from 0.01 to 10%.

11. A process according to any one of claims 1 to 10, in which the cobalt salt is used in an amount corresponding to 5—300 parts by weight of cobalt per million of parts by weight of the naphthalene or alkylnaphthalene to be hydrogenated.

12. A process according to any one of claims 1 to 11, in which the cobalt salt is a cobalt salt of a carboxylic acid having from 3 to 40 carbon atoms per molecule.

13. A process according to claim 1, substantially as hereinbefore described in any one of Examples 1, 3, 4, 6, 7, 8, 12, 13 and 14.

14. Tetrahydronaphthalene or an alkyltetrahydronaphthalene whenever manufactured by a process according to any one of the preceding claims.

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